09/976 964

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01J 17/40, H01T 1/14, H01C 7/12, H01B 1/22 — A1

(11) International Publication Number: WO 95/33278

(43) International Publication Date: 7 December 1995 (07.12.95)

(21) International Application Number: PCT/US95/06867

(22) International Filing Date: 30 May 1995 (30.05.95)

(30) Priority Data:
08/251,878 1 June 1994 (01.06.94) US

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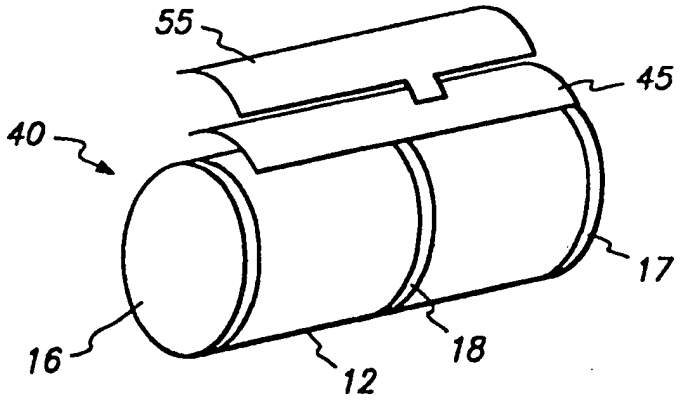
(81) Designated States: AU, BR, CA, CN, CZ, FI, JP, KR, MX, NZ, PL, RO, RU, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Published**
*With international search report.*
*Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: TELECOMMUNICATIONS GAS TUBE APPARATUS AND COMPOSITION FOR USE THEREWITH

(57) Abstract

A telecommunications gas tube apparatus (40) which is suitable for connection to a gas discharge tube (12) and which comprises an electrically non-linear resistive element (45) prepared from an electrically non-linear composition which comprises a polymeric component and a particulate filler. The composition has an initial resistivity $\rho_i$ at 25 °C of at least $10^9$ ohm-cm, and is such that a standard device containing the composition has an initial breakdown voltage $V_{Si}$, and after the standard device has been exposed to a standard impulse breakdown test, the device has a final breakdown voltage $V_{Sf}$ which is from $0.7V_{Si}$ to $1.3V_{Si}$. In addition, the composition in the device has a final resistivity $\rho_f$ at 25 °C of at least $10^9$ ohm-cm. Such compositions are useful in providing both vent-safe and fail-safe protection to a gas discharge tube (12).



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# TELECOMMUNICATIONS GAS TUBE APPARATUS AND COMPOSITION FOR USE THEREWITH

## BACKGROUND OF THE INVENTION

### Field of the Invention

This invention relates to gas discharge tube apparatus for telecommunications equipment and to compositions for use in such apparatus.

### Introduction to the Invention

Gas discharge tubes are commonly used to protect telecommunications equipment and circuits from damage in the event of electrical interference or high voltage lightning pulses. Gas tubes used in this way are often called gas tube protectors. The tubes contain a gas which ionizes at high voltages to allow electrical pulses to be directed to ground, thus minimizing any damage resulting from the pulses. If a continuing high current overload occurs, e.g. as a result of an accidental power line crossover, the tubes maintain a limited sustained ionization.

To provide protection in the event of failure from overheating during sustained over-current conditions, and to assure protection if the ionizable gas vents from the tube, gas tube protectors generally incorporate "fail-safe" and "vent-safe" mechanisms, respectively. "Fail-safe" refers to thermal damage protection, which is often provided by a fusible metal or plastic material. If the material is heated due to the energy from the current overload, it yields to a biased shorting member and provides a permanent current shunt around the gas tube. This may occur by melting a thermoplastic film positioned between two electrodes, thus allowing contact between the electrodes and shunting the

current to ground. "Vent-safe" refers to backup overvoltage protection that operates when the gas "vents" or is lost to the atmosphere. Vent-safe protection is often provided by an air-gap that is part of the external structure of the tube. The proportions of the air-gap are selected to require a firing potential considerably above, e.g. twice, the normal firing potential of the gas tube itself so that, under normal circumstances, the gas tube will prevent the air-gap from firing. This minimizes the chances that the air-gap will be damaged because although an over-voltage pulse usually fires harmlessly through a properly functioning gas tube, it may damage the air-gap which is intended as a safety backup.

To improve the reliability of air-gap vent-safe designs, it is common to environmentally isolate the air-gap to prevent contamination by moisture, air pollution, insects, or other environmental factors. Sealing materials such as encapsulants, potting compounds, conformal coatings, and gels, however, often are of limited utility as they generally cannot restrict all moisture ingress and may themselves penetrate into the air-gap, thus changing the voltage discharge levels and/or leading to corrosion. A decrease in the discharge voltage level will eventually lead to electrical shorts at low voltage levels; an increase in the discharge voltage level will defeat the purpose of the air-gap backup.

Some of these problems have been addressed by the replacement of the air-gap by a layer of solid material having particular non-linear electrical resistivity characteristics. Such an air-gap is described in co-pending, commonly assigned U.S. Patent Application No. 08/046,059 (Debbaut et al, filed April 10, 1993), the disclosure of which is incorporated herein by reference. Although environmentally stable, the solid material is subject to a decrease in breakdown voltage on successive impulses, and, in fact, during normal operation in discharging a high voltage, high energy pulse such as lightning, will be destructive to itself. Furthermore, not all such air gaps provide fail-safe protection.

## SUMMARY OF THE INVENTION

We have now found that if an electrically non-linear element prepared from an electrically non-linear material which has particular electrical properties when tested for electrical breakdown is used in place of the solid material air-gap described in U.S. Patent Application No. 08/046,059, a gas tube apparatus can be prepared which has both vent-safe and fail-safe properties. In addition, because of the nature of the non-linear material and its physical and electrical stability during successive electrical events, the apparatus can be activated repeatedly in typical telecommunication service conditions without failure of the non-linear element. Because the need to replace the element is decreased, the reliability of the telecommunications system is increased and the cost of maintenance is decreased. In a preferred embodiment, the material comprises a gel which has the ability to conform to the gas tube protector, decreasing the chance of moisture ingress, and providing increased manufacturing tolerances. Furthermore, the gel may be compatible with a gel encapsulant, thus contributing to the environmental sealing.

In a first aspect, this invention provides a telecommunications gas tube apparatus which comprises

(1) a first electrode for electrical connection to a first terminal on a gas discharge tube;

(2) a second electrode for electrical connection to a second terminal on the gas tube; and

(3) an electrically non-linear resistive element separating the first and second electrodes, said element comprising an electrically non-linear composition which

(a) comprises (i) a polymeric component, and (ii) a particulate filler,

(b) has an initial resistivity $\rho_i$ at 25°C of at least $10^9$ ohm-cm, and

(c) is such that when a standard device containing the composition has an initial breakdown voltage $V_{Si}$, and after the standard device has been exposed to a standard impulse breakdown test, the device has a final breakdown voltage $V_{Sf}$ which is from $0.7V_{Si}$ to $1.3V_{Si}$, and the composition in the device has a final resistivity $\rho_f$ at 25°C of at least $10^9$ ohm-cm.

In a second aspect, this invention provides a telecommunications gas tube apparatus which comprises

(1) a first electrode for electrical connection to a first terminal on a gas discharge tube;

(2) a second electrode for electrical connection to a second terminal on the gas tube; and

(3) an electrically non-linear resistive element separating the first and second electrodes, said element comprising an electrically non-linear composition which

(a) comprises (i) 30 to 95% by volume of the total composition gel, and (ii) 5 to 70% by volume of the total composition particulate conductive filler, and

(b) has an initial resistivity $\rho_i$ at 25°C of at least $10^9$ ohm-cm.

In a third aspect, this invention provides an assembly which comprises

(A) a retaining element; and

(B) a telecommunications gas tube apparatus of the first aspect of the invention inserted into the retaining element.

In a fourth aspect, this invention provides an electrically non-linear resistive composition of the type disclosed in the first aspect of the invention.

## BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic illustration showing a typical three-element gas discharge tube incorporated into a one pair telecommunications line;

Figure 2 is a cross-sectional view of the gas tube of Figure 1;

Figure 3 is an exploded illustration of a gas tube apparatus of the invention;

Figure 4 is a cross-sectional view of a gas tube apparatus of the invention which is encapsulated in a gel;

Figure 5 is an exploded illustration of an assembly of the invention;

Figure 6 is a cross-sectional view of the assembly of Figure 5;

Figure 7 is a schematic illustration showing a standard device for testing the compositions of the invention;

Figure 8 is a graph of impulse breakdown in volts as a function of impulse test cycles;

Figures 9 and 10 are graphs of impulse breakdown in volts as a function of the distance between electrodes for compositions of the invention; and

Figure 11 is a graph of DC breakdown voltage and impulse breakdown voltage as a function of the distance between electrodes for compositions of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

The gas tube apparatus and the assembly of the invention both comprise an electrically non-linear resistive element which comprises an electrically non-linear composition. In this specification the term "non-linear" means that the composition is substantially electrically nonconductive, i.e. has a resistivity of more than $10^9$ ohm-cm, when an applied voltage is less than the impulse breakdown voltage, but then becomes electrically conductive, i.e. has a resistivity of less than $10^9$ ohm-cm, when the applied voltage is equal to or greater than the impulse breakdown voltage. The electrically non-linear composition comprises a polymeric component and a particulate filler. The polymeric component may be any appropriate polymer, e.g. a thermoplastic material such as a polyolefin or a fluoropolymer, a thermosetting material such as an epoxy, an elastomer, a grease, or a gel. The polymeric component is generally present in an amount of 30 to 95%, preferably 35 to 90%, particularly 40 to 85% by volume of the total composition.

For many applications it is preferred that the polymeric component comprise a polymeric gel, i.e. a substantially dilute crosslinked solution which exhibits no flow when in the steady-state. The crosslinks, which provide a continuous network structure, may be the result of physical or chemical bonds, crystallites or other junctions, and must remain intact

under the use conditions of the gel. Most gels comprise a fluid-extended polymer in which a fluid, e.g. an oil, fills the interstices of the network. Suitable gels include those comprising silicone, e.g. a polyorganosiloxane system, polyurethane, polyurea, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-(ethylene/propylene)-styrene (SEPS) block copolymers (available under the tradename Septon™ by Kuraray), styrene-(ethylene-propylene/ethylene-butylene)-styrene block copolymers (available under the tradename Septon™ by Kuraray), and/or styrene-(ethylene/butylene)-styrene (SEBS) block copolymers (available under the tradename Kraton™ by Shell Oil Co.). Suitable extender fluids include mineral oil, vegetable oil such as paraffinic oil, silicone oil, plasticizer such as trimellitate, or a mixture of these, generally in an amount of 30 to 90% by weight of the total weight of the gel. The gel may be a thermosetting gel, e.g. silicone gel, in which the crosslinks are formed through the use of multifunctional crosslinking agents, or a thermoplastic gel, in which microphase separation of domains serves as junction points. Disclosures of gels which may be suitable as the polymeric component in the composition are found in U.S. Patent Nos. 4,600,261 (Debbaut), 4,690,831 (Uken et al), 4,716,183 (Gamarra et al), 4,777,063 (Dubrow et al), 4,864,725 (Debbaut et al), 4,865,905 (Uken et al), 5,079,300 (Dubrow et al), 5,104,930 (Rinde et al), and 5,149,736 (Gamarra); and in International Patent Publication Nos. WO86/01634 (Toy et al), WO88/00603 (Francis et al), WO90/05166 (Sutherland), WO91/05014 (Sutherland), and WO93/23472 (Hammond et al). The disclosure of each of these patents and publications is incorporated herein by reference.

It is preferred that the gel have a Voland hardness of 1 to 50 grams, particularly about 5 to 25 grams, especially 6 to 20 grams, have stress relaxation of 1 to 45%, preferably 15 to 40%, have tack of 5 to 40 grams, preferably 9 to 35 grams, and have an ultimate elongation of at least 50%, preferably at least 100%, particularly at least 400%, especially at least 1000%, most especially at least 1500%. The elongation is

measured according to ASTM D217, the disclosure of which is incorporated herein by reference. The Voland hardness, stress relaxation, and tack are measured using a Voland-Stevens Texture Analyzer Model LFRA having a 1000 gram load cell, a 5 gram trigger, and a 0.25 inch (6.35 mm) ball probe, as described in U.S. Patent No. 5,079,300 (Dubrow et al), the disclosure of which is incorporated herein by reference. To measure the hardness of a gel, a 20 ml glass scintillating vial containing 10 grams of gel is placed in the analyzer and the stainless steel ball probe is forced into the gel at a speed of 0.20 mm/second to a penetration distance of 4.0 mm. The Voland hardness value is the force in grams required to force the ball probe at that speed to penetrate or deform the surface of the gel the specified 4.0 mm. The Voland hardness of a particular gel may be directly correlated to the ASTM D217 cone penetration hardness using the procedure described in U.S. Patent No. 4,852,646 (Dittmer et al), the disclosure of which is incorporated herein by reference.

In addition to the polymeric component, the composition also comprises a particulate filler. The filler may be conductive, semiconductive, nonconductive, or a mixture of two or more types of fillers as long as the resulting composition has the appropriate electrical non-linearity. It is generally preferred that the filler be conductive or semiconductive. Conductive fillers generally have a resistivity of at most $10^{-3}$ ohm-cm; semiconductive fillers generally have a resistivity of at most $10^{3}$ ohm-cm, although their resistivity is a function of any dopant material, as well as temperature and other factors and can be substantially higher than $10^{3}$ ohm-cm. Suitable fillers include metal powders, e.g. aluminum, nickel, silver, silver-coated nickel, platinum, copper, tantalum, tungsten, gold, and cobalt; metal oxide powders, e.g. iron oxide, doped iron oxide, doped titanium dioxide, and doped zinc oxide; metal carbide powders, e.g. silicon carbide, titanium carbide, and tantalum carbide; metal nitride powders; metal boride powders; carbon black or graphite; and alloys, e.g. bronze and brass. Particularly preferred as fillers are

aluminum, iron oxide ($Fe_3O_4$), iron oxide doped with titanium dioxide, silicon carbide, and silver-coated nickel. If the polymeric component is a gel, it is important that the selected filler not interfere with the crosslinking of the gel, i.e. not "poison" it. The filler is generally present in an amount of 5 to 70%, preferably 10 to 65%, especially 15 to 60% by volume of the total composition.

The volume loading, shape, and size of the filler affect the non-linear electrical properties of the composition, in part because of the spacing between the particles. Any shape particle may be used, e.g. spherical, flake, fiber, or rod. Useful compositions can be prepared with particles having an average size of 0.010 to 100 microns, preferably 0.1 to 75 microns, particularly 0.5 to 50 microns, especially 1 to 20 microns. A mixture of different size, shape, and/or type particles may be used. The particles may be magnetic or nonmagnetic.

In addition to the particulate filler, the composition may comprise other conventional additives, including stabilizers, pigments, crosslinking agents, catalysts, and inhibitors.

The compositions of the invention may be prepared by any suitable means, e.g. melt-blending, solvent-blending, or intensive mixing, and may be shaped by conventional methods including extrusion, calendaring, casting, and compression molding. If the polymeric component is a gel, the gel may be mixed with the filler by stirring and the composition may be poured or cast onto a substrate or into a mold to be cured, often by the addition of heat.

The compositions of the invention have excellent stability as measured both by resistivity and breakdown voltage. The compositions are electrically insulating and have an initial resistivity $\rho_i$ at 25°C of at least $10^9$ ohm-cm, preferably $10^{10}$ ohm-cm, particularly $10^{11}$ ohm-cm, especially

$10^{12}$ ohm-cm. The initial resistivity value $\rho_i$ is such that when the composition is formed into a standard device as described below, the initial insulation resistance $R_i$ is at least $10^9$ ohms, preferably at least $10^{10}$ ohms, particularly at least $10^{11}$ ohms. An $R_i$ value of at least $10^9$ ohms is preferred when the compositions of the invention are used in telecommunications apparatus. After being exposed to the standard impulse breakdown test, described below, the final resistivity $\rho_f$ at 25°C is at least $10^9$ ohm-cm, and the ratio of $\rho_f$ to $\rho_i$ is at most $1 \times 10^3$, preferably at most $5 \times 10^2$, particularly at most $1 \times 10^2$, especially at most $5 \times 10^1$, most especially at most $1 \times 10^1$. The final insulation resistance $R_f$ for a standard device after exposure to the standard impulse breakdown test is at least $10^9$ ohms, preferably at least $10^{10}$ ohms, particularly at least $10^{11}$ ohms.

When the composition of the invention is formed into a standard device as described below and exposed to a standard impulse breakdown test, the device has an initial breakdown voltage $V_{Si}$ and a final breakdown voltage $V_{Sf}$ which is from $0.70V_{Si}$ to $1.30V_{Si}$, preferably from $0.80V_{Si}$ to $1.20V_{Si}$, particularly from $0.85V_{Si}$ to $1.15V_{Si}$, especially from $0.90V_{Si}$ to $1.10V_{Si}$. The value of the breakdown voltage is affected by the volume fraction of the particulate filler, by the particle size, and by the distance between the particles among other factors. In general, as particle size decreases, the breakdown voltage increases.

Some compositions of the invention will "latch", i.e. remain in a conductive state with a resistivity of less than $10^6$ ohm-cm, after one voltage discharge. If the latched device is made from a composition comprising a gel, the device can be "reset" into a high resistivity state, i.e. a resistivity of at least $10^9$ ohm-cm, by physical deformation, e.g. flexing, torsion, compression, or tension. The latching behavior is a function of particle size, interparticle spacing, and particle shape. In gels, generally small

spherical particles, e.g. 1 to 5 microns, with a small interparticle spacing, e.g. less than 4 microns, will latch.

Under certain electrical conditions, compositions of the invention, particularly compositions comprising aluminum, will provide fail-safe protection. If exposed to a sufficiently high energy level, e.g. 30A and 1000 volts for a time of 2 seconds to 30 minutes, the particulate filler can fuse together and provide a permanent conductive path between the electrodes, giving a final resistance of less than 10 ohms, e.g. 1 to 10 milliohms. Such behavior is desirable in the event of crossed power lines and results in a permanent short circuit.

The invention is illustrated by the drawing in which Figure 1 is a schematic illustration of a conventional telecommunications circuit 10 which incorporates a gas tube 12 in a telecommunications line. The gas tube 12, which is shown in cross-section in Figure 2, has a first terminal 16 and a second terminal 17 for connection to the tip side 13 and the ring side 14, respectively, of the telecommunications circuit. In addition, the gas tube 12 has a center ground terminal 18. A ceramic shell 19 encloses an ionizable gas 20 which ionizes to form a discharge plasma at a given voltage.

Figure 3 is an exploded view of a gas tube apparatus 40 of the invention. In this embodiment, the first terminal 16 and the second terminal 17 of the gas tube 12 also function as first and second electrodes, respectively, for the gas tube apparatus 40. (Although not shown, the gas tube may comprise a third terminal which may be connected to a third electrode in the gas tube apparatus. One of the electrodes may be a grounding electrode.) Electrically non-linear resistive element 45 is positioned in contact with first terminal 16 and second terminal 17. Ground electrode 55 is in physical contact with resistive element 45, and is in electrical contact with ground terminal 18 of gas tube 12. In a preferred embodiment, the non-linear composition comprising

the resistive element has sufficient flexibility that it conforms to the shape of gas tube 12.

Figure 4 shows a cross-sectional view of gas tube apparatus 40 embedded in a gel encapsulant 50. The encapsulant, which may be, e.g. a potting compound, a conformal coating, or a gel, provides environmental protection from moisture and other contaminants. In addition, the encapsulant may exclude oxygen from the plasma discharge, and act as a heat sink to draw thermal energy away from local hot spots. It is preferred that the resistive element be chemically inert to the encapsulant.

Figure 5 is an exploded view of an assembly 70 of the invention and Figure 6 is a cross-sectional view of that assembly. Retaining element 72 is designed to contain gas tube 12, resistive element 45, and a ground electrode 55'. Although the resistive element 45 may be laminar as shown, to enhance contact with gas tube 12 the resistive element may be curved or otherwise shaped. Spring leads 76,78 are attached to gas tube 12 and serve to make electrical contact with respective insulation displacement connectors (not shown). Gas tube 12 is held in the appropriate position with the resistive element 45 and ground electrode 55' by means of retaining element 72, retainer cap 74, and grounding pin 80 which can be inserted into a recess or hole in retainer cap 74. Retainer cap 74 may be ultrasonically welded, glued, or otherwise fused to retaining element 72. To maintain the proper distance between the gas tube 12 and ground electrode 55', spacer 56 protrudes from ground electrode 55'. The height of spacer 56 can be selected to achieve different levels of voltage breakdown. The retaining element 72 may be filled with the encapsulant to surround the contents.

The invention is illustrated by the following examples.

Examples 1 to 14

The ingredients listed in Table I were mixed with a tongue depressor to disperse the particulate filler, degassed in a vacuum oven for one minute, poured onto a PTFE-coated release sheet and cured. A Standard Device, described below, was prepared with an electrode spacing of 1 mm. Samples were then subjected to one of three tests, although the Standard Impulse Breakdown Test was extended for several samples from 5 to 100 cycles. The results, shown in Figures 8 to 11, indicated that the compositions based on silicone gel 1 and thermoplastic gel had excellent stability and reproducibility over 100 cycles based on impulse breakdown and insulation resistance. The composition based on silicone gel 2 showed a decrease in insulation resistance to less than $10^5$ ohms by about 41 cycles. The composition based on a silicone grease showed a similar decrease by four cycles (Figure 8). Example 5, based on an epoxy, shattered under the impulse test conditions, but showed a decrease in insulation resistance by 15 cycles under DC breakdown testing. Figures 9 and 10 show the effect of particle size and filler loading on the impulse breakdown voltage for samples which ranged in thickness from 0.25 to 1.0 mm. Figure 11 shows that for a given particle size and loading, the impulse breakdown and the DC breakdown voltage were comparable.

Standard Device

A circular sample with a diameter of 11.2 mm (i.e. a surface area of about 1 $cm^2$) and a thickness of 1 mm was cut from the cured composition and inserted into the test fixture shown in cross-section in Figure 7. The test composition sample 90 was positioned between two circular aluminum electrodes 91,92, each with a diameter of about 11.2 mm and a surface in contact with the composition 90 of about 100 $mm^2$. Polycarbonate sleeve 93 with an inner diameter of slightly more than 11.2 mm was positioned over the assembled electrodes and composition and the assembly was inserted into fixture 94

containing support elements 95,96. Micrometer 97 was adjusted until the spacing between the electrodes 91,92 was 1 mm. (For the Modified Impulse Breakdown Test described below, the micrometer was adjusted to vary the electrode spacing, i.e. the sample thickness, from 0.25 to 1.0 mm. For gel samples, the sample had an initial thickness of 1 mm. When the micrometer was adjusted to decrease the sample thickness, excess composition flowed through opening 98 in electrode 94 and between electrodes 91,92 and polycarbonate sleeve 93.)

Standard Impulse Breakdown Test

A standard device, with dimensions of 1 $cm^2$ x 1 mm was inserted into the test apparatus shown in Figure 7. Prior to testing, the insulation resistance $R_i$ for the device was measured at 25°C with a biasing voltage of 50 volts using a Genrad 1863 Megaohm meter; the initial resistivity $\rho_i$ was calculated. The device was inserted into a circuit with an impulse generator and for each cycle a high energy impulse with a 10 x 1000 $\mu$s waveform (i.e. a rise time to maximum voltage of 10 $\mu$s and a half-height at 1000 $\mu$s) and a current of at most 1A was applied. The peak voltage measured across the device at breakdown, i.e. the voltage at which current begins to flow through the gel, was recorded as the impulse breakdown voltage. For the Standard Impulse Breakdown Test, five cycles were conducted. The final insulation resistance $R_f$ after five cycles for the standard test was measured and the final resistivity $\rho_f$ was calculated.

Modified Impulse Breakdown Test

Samples were prepared with electrode spacing varying from 0.25 to 1 mm and were tested following the procedure of the Standard Impulse Breakdown Test.

DC Breakdown Test

A standard device was inserted into a circuit and was subjected to a voltage which increased at a rate of 200 volts/second (Hipot Model M1000 DC Tester). The DC breakdown was recorded as the voltage at which 5 milliamps of current began to flow through the device.

TABLE I

| Example | Polymer | Al Filler | | Test | $R_i$ (Ω) | $R_f$ (Ω) | Test Cycles |
|---|---|---|---|---|---|---|---|
| | | Size (μm) | Vol. % | | | | |
| 1 | Silicone gel 1 | 20 | 40.0 | I1 | $10^{12}$ | $10^{12}$ | 100 |
| 2 | Thermoplastic gel | 20 | 35.1 | I1 | $10^{12}$ | $10^{12}$ | 100 |
| 3 | Silicone grease | 20 | 26.4 | I1 | $10^{12}$ | $<10^5$ | 4 |
| 4 | Silicone gel 2 | 20 | 40.0 | I1 | $10^{10}$ | $<10^5$ | 46 |
| 5 | Epoxy | 20 | 26.4 | D* | $10^{10}$ | $<10^5$ | 15 |
| 6 | Silicone gel 1 | 1-5 | 45.6 | I2,D | | | |
| 7 | Silicone gel 1 | 1-5 | 40.0 | I2 | | | |
| 8 | Silicone gel 1 | 1-5 | 35.1 | I2 | | | |
| 9 | Silicone gel 1 | 1-5 | 26.4 | I2 | | | |
| 10 | Silicone gel 1 | 20 | 45.6 | I2,D | | | |
| 11 | Silicone gel 1 | 20 | 35.1 | I2 | | | |
| 12 | Silicone gel 1 | 20 | 26.4 | I2 | | | |
| 13 | Silicone gel 1 | 20 | 19.3 | I2 | | | |
| 14 | Silicone gel 1 | 20 | 13.3 | I2** | | | |

Notes to Table:

Silicone gel 1 was a mixture of 0.8 parts of a first composition composed of 26% by weight Nusil Ply™ 7520 CS 170 divinyl terminated polydimethylsiloxane (available from McGhan-Nusil), 73.88% Carbide L45/50 CS polydimethylsiloxane silicone fluid diluent (available from Union Carbide), 0.1% Nusil Cat™ 50 catalyst (3 to 4% platinum in silicone oil, available from McGhan-Nusil), and 0.02% T2160 inhibitor (1,3,5,7-tetravinyltetramethylcyclotetrasiloxane, available

from Huls) and 1.0 parts of a second composition composed of 26% by weight Nusil Ply™ 7520 CS 170 polydimethylsiloxane, 73.91% Carbide L45/50 CS silicone fluid diluent, and 0.9% T1915 tetrakisdimethylsiloxysilane crosslinking agent (available from Huls).

Thermoplastic gel contained 10% by weight Septon™ 4055 styrene-(ethylene/propylene)-styrene block copolymer having an ethylene/propylene midblock and a molecular weight of 308,000 (available from Kuraray), 87.5% Witco™ 380 extender oil (available from Witco), and 1% Irganox™ B900 antioxidant (available from Ciba-Geigy).

Silicone grease was a mixture of silicon dioxide and 50 cst silicone oil with the $SiO_2$ added until the silicone oil would no longer flow under its own weight.

Silicone gel 2 was SylGard™ Q3-6636 silicone dielectric gel (available from Dow Corning).

Epoxy was ACE™ 18612 5-minute epoxy (available from Ace Hardware Stores).

Aluminum powder with an average particle size of 20 microns and a substantially spherical shape was product type 26651, available from Aldrich Chemicals.

Aluminum powder with an average particle size of 1 to 5 microns (passed 325 mesh) and a substantially spherical shape was product type 11067, available from Johnson Mathey.

I1 is the Standard Impulse Breakdown Test.

I2 is the Modified Impulse Breakdown Test.

D is the DC Breakdown Test.

Examples 15 to 18

To determine whether compositions of the invention would remain in a conducting condition after a voltage discharge, standard devices with the compositions shown in Table II were prepared. The initial resistance was measured prior to exposing the device to one voltage discharge of the type described in the Standard Impulse Breakdown Test above. After the discharge the final resistance was measured. A device was deemed to have latched if the final resistance was less than

$10^5$ ohms. The approximate spacing between particles was calculated using the formula $\lambda = 4(1-f)r/(3f)$, where $\lambda$ is the mean free path (i.e. the interparticle spacing), f is the volume fraction of particles, and r is the particle radius. Whether the composition latched was a function of both the particle size and loading of the particles. The 20 micron aluminum latched at a higher interparticle spacing, apparently in part because not all the particles were completely spherical although the particles on average were substantially spherical.

TABLE II

| Example | Polymer | Al Filler | | Latched | Interparticle Spacing $\lambda$ ($\mu$m) |
|---|---|---|---|---|---|
| | | Size ($\mu$m) | Vol. % | | |
| 15 | Silicone gel | 1-5 | 26.4 | No | 5.6 |
| 16 | Silicone gel | 1-5 | 35.1 | Yes | 3.7 |
| 17 | Silicone gel | 20 | 35.1 | No | 24.6 |
| 18 | Silicone gel | 20 | 45.6 | Yes | 15.9 |

What is claimed is:

1. A non-linear resistive composition which

(a) comprises (i) a polymeric component, and (ii) a particulate filler,

(b) has an initial resistivity $\rho_i$ at 25°C of at least $10^9$ ohm-cm, and

(c) is such that when a standard device containing the composition has an initial breakdown voltage $V_{Si}$, and after the standard device has been exposed to a standard impulse breakdown test, the device has a final breakdown voltage $V_{Sf}$ which is from $0.7V_{Si}$ to $1.3V_{Si}$, and the composition in the device has a final resistivity $\rho_f$ at 25°C of at least $10^9$ ohm-cm.

2. A composition according to claim 1 wherein the polymeric component comprises a gel.

3. A composition according to claim 2 wherein the gel is a thermosetting gel or a thermoplastic gel.

4. A composition according to claim 1 wherein the particulate filler comprises a conductive or a semiconductive filler.

5. A composition according to claim 4 wherein the particulate filler is selected from the group consisting of metal powders, metal oxide powders, metal carbide powders, metal nitride powders, and metal boride powders.

6. A composition according to claim 5 wherein the particulate filler comprises aluminum, nickel, silver, silver-coated nickel, platinum, copper, tantalum, tungsten, iron

oxide, doped iron oxide, doped zinc oxide, silicon carbide, titanium carbide, or tantalum carbide.

7. A composition according to claim 1 or 2 wherein $V_{Sf}$ is from $0.8V_{Si}$ to $1.2V_{Si}$.

8. An composition according to claim 1 or 2 wherein the ratio of $\rho_i$ to $\rho_f$ is at most $10^3$.

9. An composition according to claim 1 or 2 wherein the initial resistivity $\rho_i$ is at least $10^{11}$ ohm-cm.

10. An composition according to claim 1 or 2 wherein the particulate filler has a substantially spherical shape.

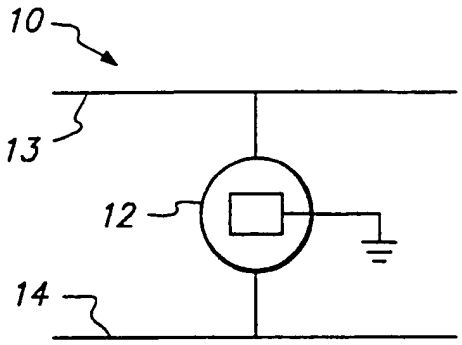


FIG. 1

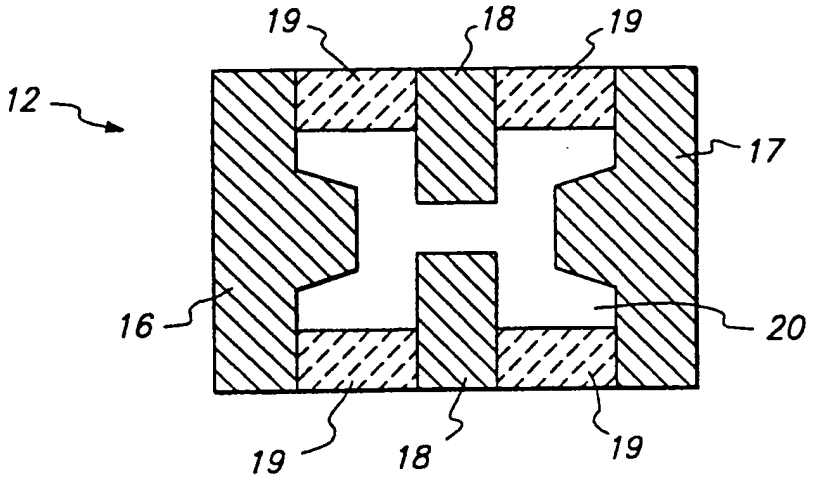


FIG. 2

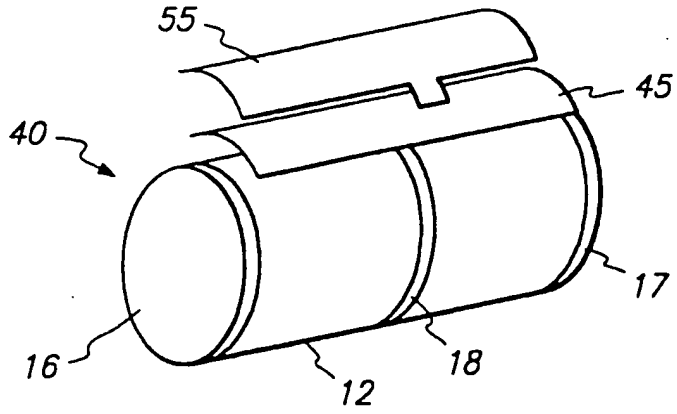


FIG. 3

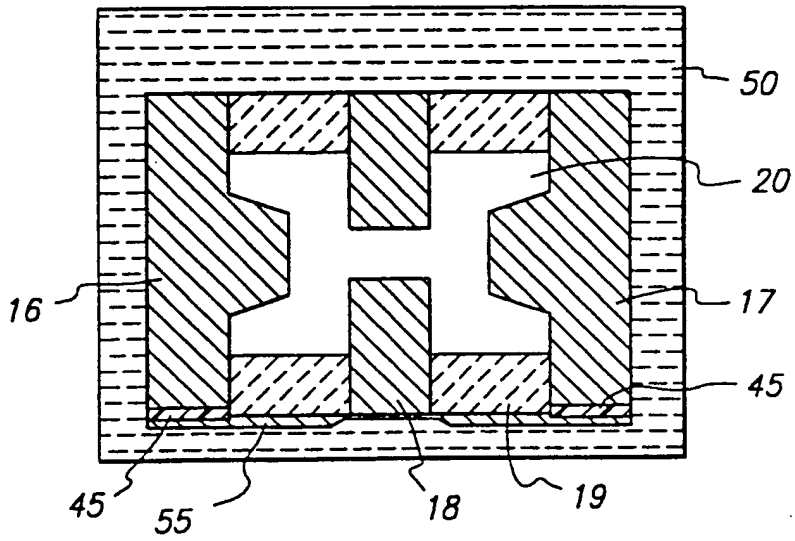


FIG. 4

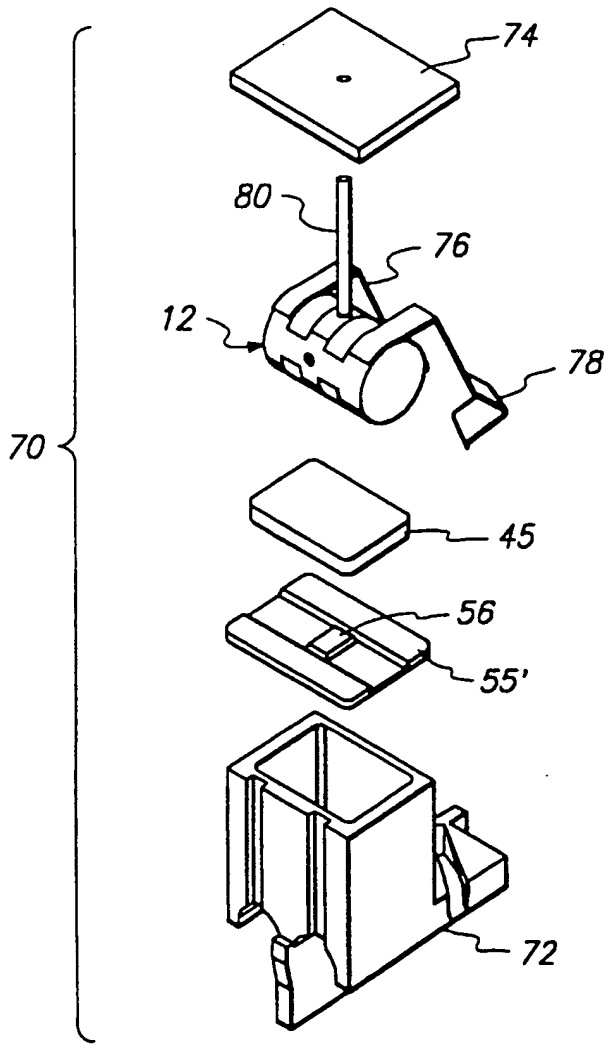


FIG. 5

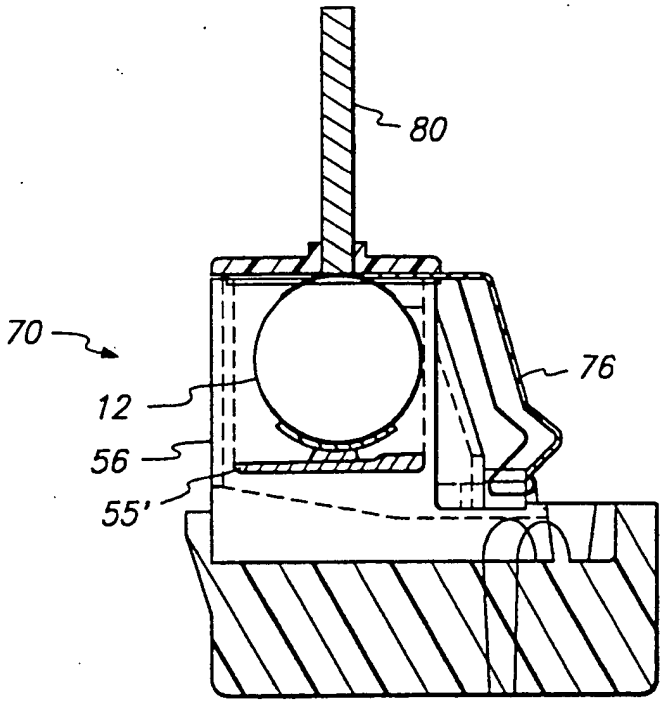


FIG. 6

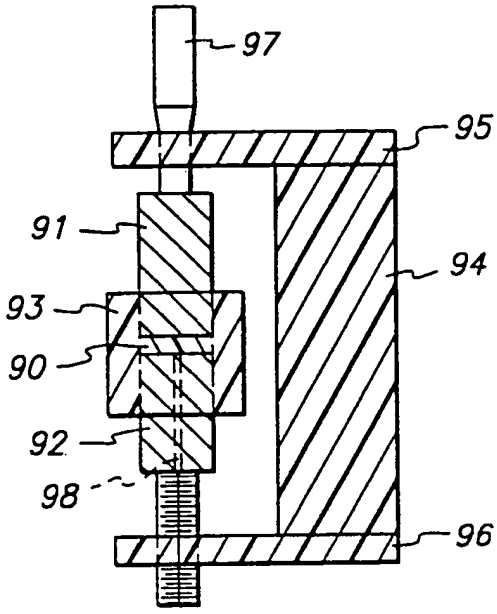


FIG. 7

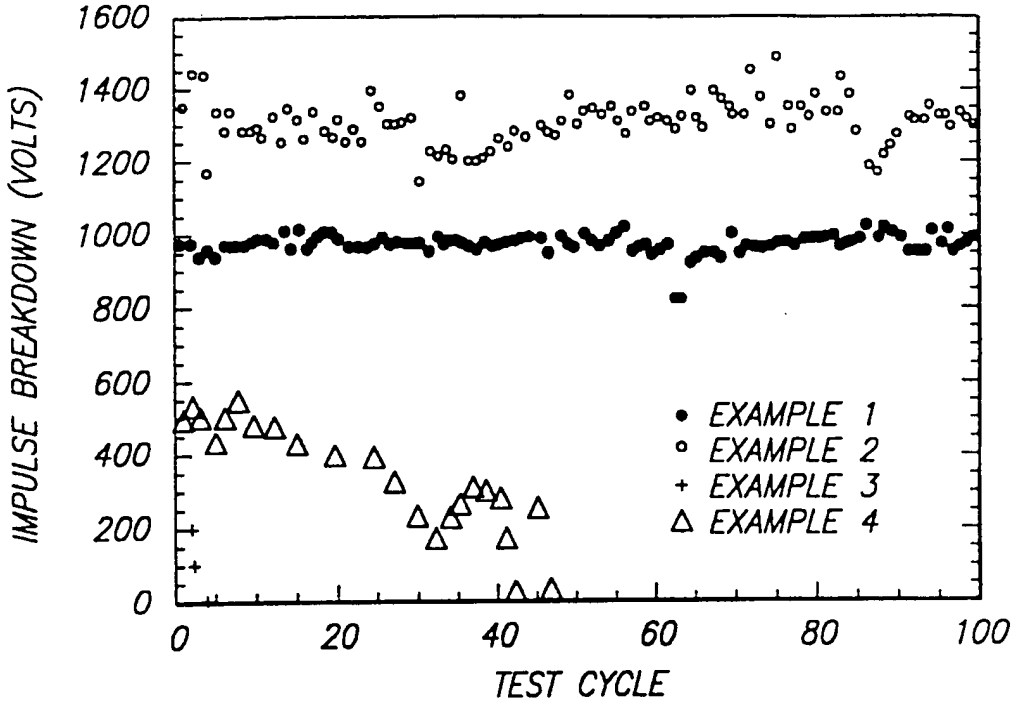
IMPULSE BREAKDOWN (VOLTS)
1600
1400
1200
1000
800
600
400
200
0
0
20
40
60
80
100
TEST CYCLE
EXAMPLE 1
EXAMPLE 2
EXAMPLE 3
EXAMPLE 4

FIG.8

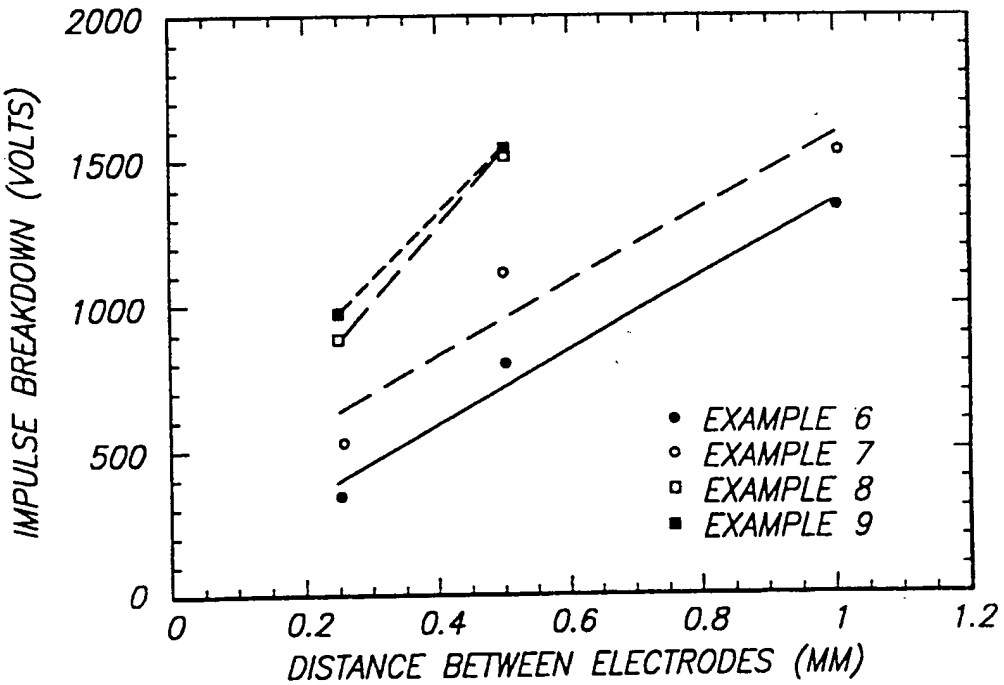
IMPULSE BREAKDOWN (VOLTS)
2000
1500
1000
500
0
0
0.2
0.4
0.6
0.8
1
1.2
DISTANCE BETWEEN ELECTRODES (MM)
EXAMPLE 6
EXAMPLE 7
EXAMPLE 8
EXAMPLE 9

FIG. 9

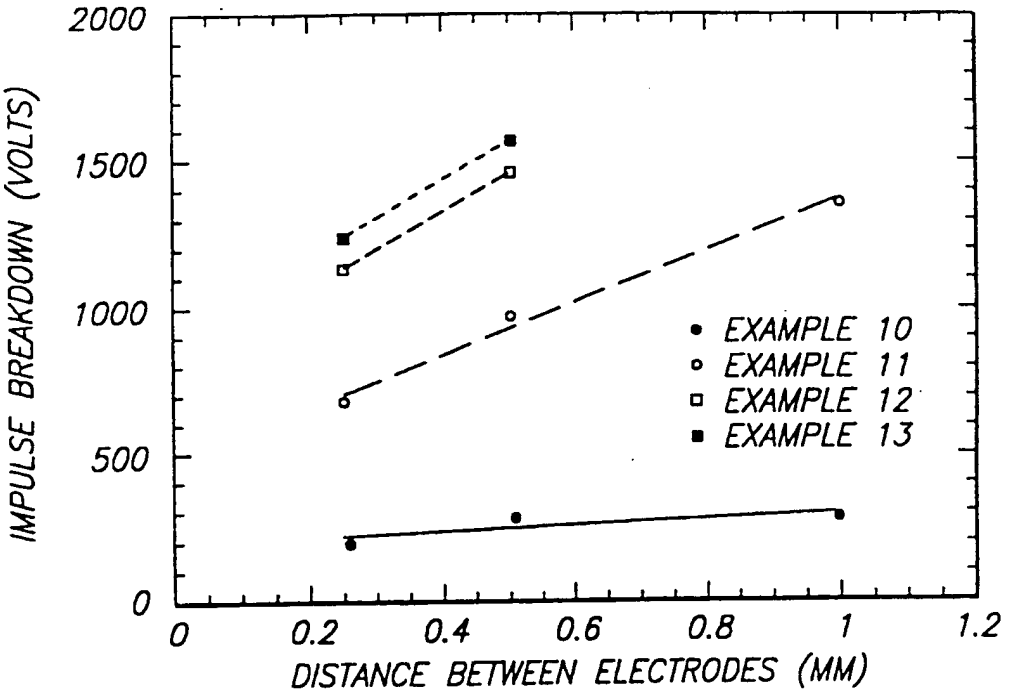
IMPULSE BREAKDOWN (VOLTS)
2000
1500
1000
500
0
0
0.2
0.4
0.6
0.8
1
1.2
DISTANCE BETWEEN ELECTRODES (MM)
EXAMPLE 10
EXAMPLE 11
EXAMPLE 12
EXAMPLE 13

FIG. 10

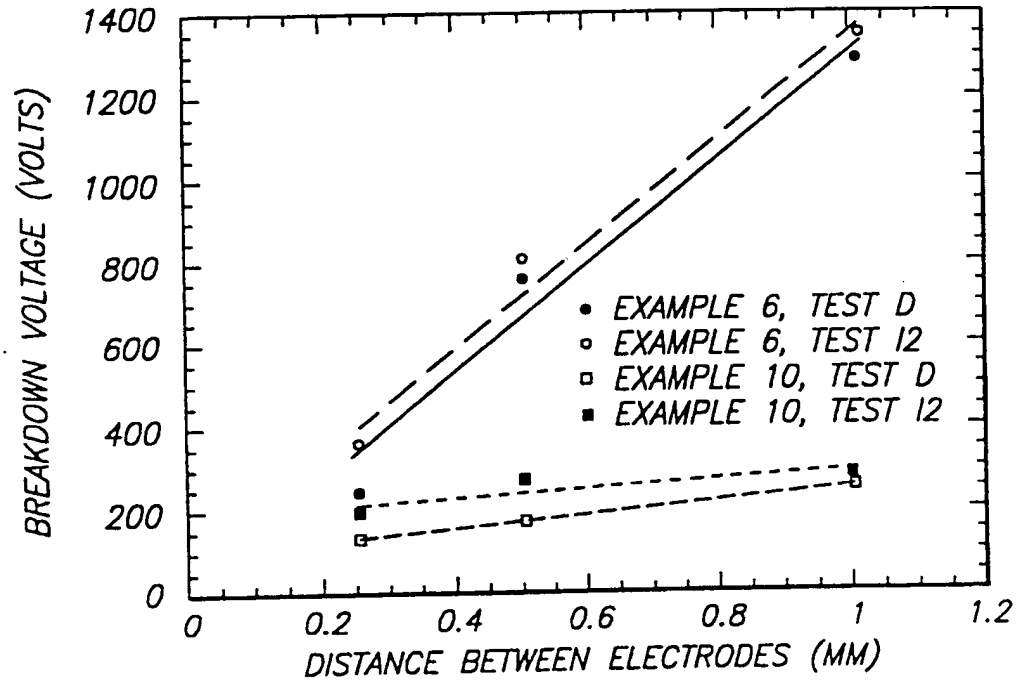
BREAKDOWN VOLTAGE (VOLTS)
1400
1200
1000
800
600
400
200
0
0
0.2
0.4
0.6
0.8
1
1.2
DISTANCE BETWEEN ELECTRODES (MM)
EXAMPLE 6, TEST D
EXAMPLE 6, TEST I2
EXAMPLE 10, TEST D
EXAMPLE 10, TEST I2

FIG. 11

# INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 95/06867

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01J17/40 H01T1/14 H01C7/12 H01B1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01J H01T H01B H01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO,A,94 00856 (RAYCHEM CORP) 6 January 1994<br>see page 8, line 26 - page 11, line 35;<br>figures 5-9 | 1-6 |
| A | US,A,3 950 604 (PENNECK RICHARD J) 13 April 1976<br>see abstract; examples | 1-6 |
| A | US,A,4 992 333 (HYATT HUGH M) 12 February 1991<br>see column 4, line 54 - line 58<br>see column 5, line 10 - column 7, line 22 | 1-6 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 4 October 1995 | 13. 10. 95 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016 | Authorized officer<br>Schaub, G |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter[illegible]al Application No
PCT/US 95/06867

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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| | | CN-A- | 1085691 | 20-04-94 |
| | | EP-A- | 0649563 | 26-04-95 |
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| | | FR-A,B | 2198226 | 29-03-74 |
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| | | AU-B- | 4444489 | 24-05-90 |
| | | CA-A- | 2001740 | 18-05-90 |
| | | EP-A- | 0369826 | 23-05-90 |
| | | JP-A- | 2152204 | 12-06-90 |